Resonant X-ray emission study of the lower-mantle ferropericlase at high pressures

JUNG-FU LIN,†,* ZHU MAO,† IGNACE JARRIGE,‡ YUMING XIAO,§ PAUL CHOW,‖ TAKUO OKUCHI,¶ NOZOMU HIRAOKA,# AND STEVEN D. JACOBSEN**

†Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, Austin, Texas 78712, U.S.A.
‡Synchrotron Radiation Research Unit, Japan Atomic Energy Agency, Hyogo 679-5148, Japan
§HPCAT, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, U.S.A.
‖Institute for Study of the Earth’s Interior, Okayama University, Yamada 827, Misasa, Tottori 682-0193, Japan
¶National Synchrotron Radiation Research Center, Hsinchu 30077, Taiwan
#Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois 60208, U.S.A.

ABSTRACT

Electronic states of iron in Earth’s mantle minerals including ferropericlase, silicate perovskite, and post-perovskite have been previously investigated at high pressures and/or temperatures using various experimental techniques, including X-ray emission and Mössbauer spectroscopies. Although such methods have been used to infer changes in the electronic spin and valence states of iron in lower mantle minerals, they do not directly probe the 3d electronic states quantitatively. Here we use 1s2p resonant X-ray emission spectroscopy (RXES) at the Fe K pre-edge to directly probe and assess the 3d electronic states and the crystal-field splittings of Fe2+ in the lower-mantle ferropericlase [(Mg0.75Fe0.25)O] at pressures up to 90 GPa. The pre-edge features from X-ray absorption spectroscopy in the partial fluorescence yield (PFY-XAS) and RXES results explicitly show three excited states for high-spin Fe2+ (a lower-energy 4T_{1g} state, a 4T_{2g} state, and a higher-energy 4T_{1u} state) and a single 5D_{5/2} state for low-spin Fe2+, attributed to the (t_{2g})^6(e_g)^1 excited configuration. This latter feature begins to appear at 48 GPa and grows with pressure, while the peaks related to high-spin Fe2+ vanish above 80 GPa. The observed pre-edge features are consistent with purely quadrupolar transitions resulting from the centrosymmetric character of the Fe2+ site. The K pre-edge RXES spectra at the incident energy of 7112 eV, which are similar to the Fe L-edge spectra, are also used successfully to quantitatively obtain consistent results on the spin transition of Fe2+ in ferropericlase under high pressures. Owing to the superior sensitivity of the RXES technique, the observed electronic states and their energy separations provide direct information on the local electronic structures and crystal-field splitting energies of the 3d electronic shells of Fe2+ in ferropericlase at relevant pressures of the Earth’s lower mantle.

Keywords: Ferropericlase, diamond anvil cell, spin transition, resonant X-ray emission spectroscopy, partial fluorescence yield, high pressures

INTRODUCTION

Electronic states of iron, including total spin momentum and valence charge, have been studied extensively at high pressures in lower-mantle ferropericlase, silicate perovskite, and post-perovskite, owing to their influence on a range of physical properties relevant to understanding the state and dynamics of the Earth’s deep interior (e.g., Badro et al. 2003, 2004; Catalli et al. 2010; Grocholski et al. 2009; Jackson et al. 2005; Lin et al. 2005, 2008; Lin and Tsuchiya 2008; McCammon et al. 2008; Persson et al. 2006; Tsuchiya et al. 2006). In particular, a high-spin to low-spin transition of Fe2+ has been reported in ferropericlase [(Mg,Fe)O] at high pressures using Mössbauer spectroscopy (Speziale et al. 2005; Gavriliuk et al. 2006; Kantor et al. 2006; Lin et al. 2006, 2009; Lyubutin et al. 2009), X-ray emission spectroscopy (XES) (Badro et al. 2003; Lin et al. 2005, 2007), and optical absorption spectroscopy (Goncharov et al. 2006; Keppler et al. 2007). These techniques have long played important and complementary roles in studying the electronic structures of planetary materials in extreme environments.

Although many experimental techniques allow inference of changes in spin and valence states by measuring electrical, optical, vibrational, magnetic, or structural properties, few directly probe the 3d electronic states quantitatively (e.g., Lin and Tsuchiya 2008). For example, XES and Mössbauer spectroscopy probe processes occurring in the inner electronic shell (in XES) or in the nuclei of iron ions (in Mössbauer) as indicators of the electronic spin transitions that occur in the outermost 3d orbitals of the iron ions (Maddock 1997; Vankó et al. 2006). Mössbauer spectroscopy has been widely used to investigate spin transitions of iron in lower-mantle minerals owing to its sensitivity to the hyperfine parameters of iron nuclei, which can reflect the redistribution of 3d electrons across the spin transitions (Maddock 1997). In XES, the Fe Kβ′ satellite peak arising from the 3p-3d electronic exchange interaction is sensitive to the local magnetic moment of the dilute iron-containing minerals, but it does not necessarily distinguish between various valence states or coordination numbers. Furthermore, the intensity of the Kβ′ satellite peak is a complex function of many factors, from which the